crop and Tos. I, 45–47°; run 17, 1st crop and Bros. IIA, 44–56°; run 17, 1st crop and Tos. IIA, 39–41°; run 17, 2nd crop and Bros. IIA, 43–54°; run 17, 2nd crop and Tos. IIA, 40–42°. In run 17, the first crop gave oils when mixed with Bros. I, Bros. IB, Tos. IB or Tos. I; the second crop gave oils with Bros. I, Bros. IB, Tos. IB and Tos. I.

Control Experiments.—Demonstration of the complete separation of the olefinic and alcoholic products was accomplished by mixing 2 parts of IA alcohol $\alpha^{25}\mathrm{D}$ +31.5° (l = 1 dm.) with one part of an equimolar mixture of the four 2-phenyl-2-butenes and by submitting the resulting mixture (3.0 g.) to the chromatographic separation described above, followed by distillation of each fraction: alcohol fraction, $\alpha^{23}\mathrm{D}$ +31.6° (l = 1 dm.); olefin fraction, $\alpha^{23}\mathrm{D}$ 0.02° (l = dm.). Thus there is no detectable contamination of olefin with alcohol, and less than 0.1% contamination of alcohol with olefin.

To ascertain whether experiments 12 and 13 were carried out in the presence of base, a large excess of finely divided potassium carbonate was refluxed for four hours with 500 ml. of dry acetonitrile, the mixture was filtered quickly while still at the boiling temperature, and the solvent was removed by distillation. No weighable residue remained in the flask. Water was added to the flask and titration of the resulting solution with dilute acid gave no more acid consumption than a blank run. It can be concluded that the reaction was conducted in the absence of base. To determine whether secondary acetate could be produced from olefin, and whether the acetates of 3-phenyl-2-butanol once formed were stable under the conditions of the acetolysis, a mixture of 2 g. of the acetate of IA ($\alpha^{23}\mathrm{D}$ −8.08°, l = 1 dm.) 1 g. of *cis*-2-phenyl-2-butene[4] and 1 g. of *trans*-2-phenyl-2-butene[4] and 1 g. of 3-phenyl-1-butene[4] were held at 75° in the acetic acid solvolysis mixture for 36 hours. The acetate–olefin mixture that was recovered was reduced with lithium aluminum hydride, the alcohol and olefin separated (see above procedure), and the alcohol recovered ($\alpha^{23}\mathrm{D}$ +31.5°, l = 1 dm.), wt. 1.48 g.

Acknowledgment.—It is a pleasure to acknowledge stimulating and helpful discussions of problems related to this paper with Drs. W. G. McMillan, K. N. Trueblood and G. S. Hammond.

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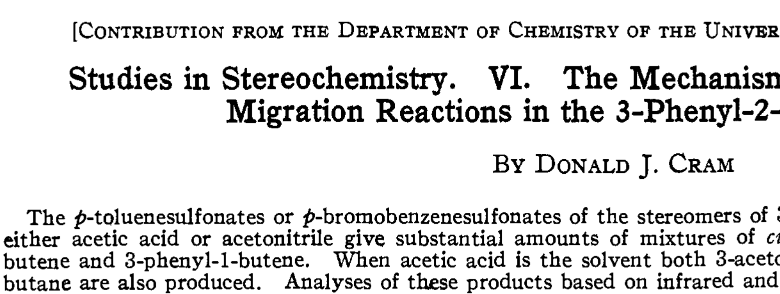
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies in Stereochemistry. VI. The Mechanisms of the E_1 and Hydrogen Migration Reactions in the 3-Phenyl-2-butanol System

BY DONALD J. CRAM

The *p*-toluenesulfonates or *p*-bromobenzenesulfonates of the stereomers of 3-phenyl-2-butanol when allowed to react in either acetic acid or acetonitrile give substantial amounts of mixtures of *cis*- and *trans*-2-phenyl-2-butene, 2-phenyl-1-butene and 3-phenyl-1-butene. When acetic acid is the solvent both 3-acetoxy-2-phenylbutane and 2-acetoxy-2-phenylbutane are also produced. Analyses of these products based on infrared and polarimetric methods have been developed. The simple E_1 reaction has been shown to go by at least two mechanisms: one stereospecific and *trans* in steric direction, the other non-stereospecific. The migration of a hydrogen from carbon-3 to carbon-2 in the 3-phenyl-2-butanol system has been demonstrated to be a transformation concomitant to the simple elimination and solvolysis reactions. This rearrangement has been shown to be intramolecular, and to involve a symmetric intermediate, probably the methylethylphenylcarbonium ion. A comparison of the abilities of hydrogen and phenyl to participate in an intramolecular displacement reaction has been made, and these abilities have been correlated with the geometry of the transition states for the reactions involved.

In the preceding paper of this series evidence was adduced for the existence of a phenonium sulfate ion-pair as a discrete intermediate intervening between the starting *p*-toluenesulfonates of the isomers of 3-phenyl-2-butanol and their non-olefinic solvolysis products (acetates).[1] The present investigation is concerned with the mechanism by which the 2-phenylbutenes come into being as an accompanying set of products of the same starting materials.



The use of the 3-phenyl-2-butanol system for the study of the E_1 reaction (and accompanying rearrangement–elimination reactions) offers several unique and distinct advantages over systems that have been used in the past for analogous studies.[2] The presence of two asymmetric carbon atoms in the starting material and the existence of *cis* and *trans* isomerism in the 2-phenyl-2-butene products allows a determination of the stereochemistry of the E_1 reaction. Carbon atoms two and three are not part of a ring structure, and hence each stereomeric starting material can assume whatever rotational conformation is the most compatible with the steric requirements of the elimination reaction. An examination of the stereochemistry of the hydrogen migration is possible through a comparison of the configuration of the starting material and that of the 2-acetoxy-2-phenylbutane which is produced (along with 2-phenyl-1-butene) as a product of rearrangement. A

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[1] D. J. Cram, THIS JOURNAL, **74**, 2129 (1952).

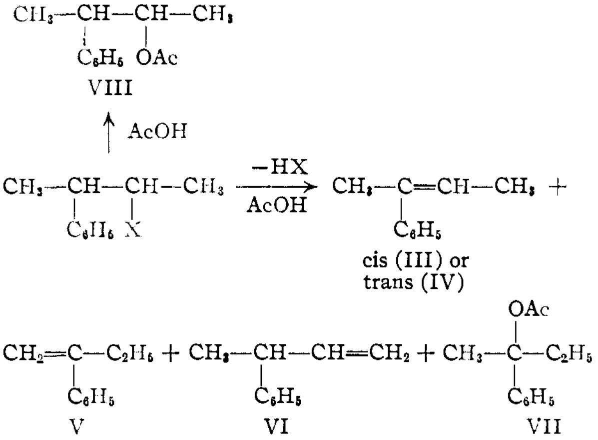
[2] The conclusion of C. C. Price and J. V. Karabinos [*ibid.*, **62**, 1159 (1940)] that a predominantly *trans* elimination of the elements of water occurs when either *cis*- or *trans*-2-phenylcyclohexanol is heated with phosphoric acid has become somewhat equivocated by the recent findings of E. R. Alexander and A. Mudrak [*ibid.*, **72**, 1810 (1950)] that the 3-phenylcyclohexene used in the former investigation as a standard was contaminated with a considerable amount of 1-phenylcyclohexene. If the index of refraction for 3-phenylcyclohexene obtained by the latter investigators is applied to the data of Price, *et al.*, it appears that when conjugated olefin can be produced by a *trans* elimination, the reaction largely assumes such a course (88% conjugated, 12% unconjugated olefin). However, when the conjugated olefin cannot be formed by a *trans* elimination reaction, *cis* elimination accounts for about half the product, the steric course of the reaction giving rise to the rest of the product not being clear. If one takes into consideration the probability that both the phenyl and hydrogen become involved in migrations from one carbon to the other in a manner analogous to those found in the 3-phenyl-2-butanol system (ref. 1), few conclusions can be reached without a thorough study of the immediate precursors of the two phenylcyclohexenes.

TABLE I

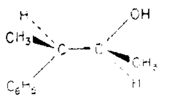
PHYSICAL PROPERTIES AND ANALYSES OF STARTING MATERIALS AND PRODUCTS

Number	Compound	n^{25}_D	M.p., °C.	Rotation	Mol. form	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
..	IA *p*-Bromobenzenesulfonate[a]	....	74–75[b]	$[\alpha]^{21}_D$ +21.5°[c]	$C_{16}H_{17}O_3SBr$	52.03	51.90	4.93	4.77
..	IIB *p*-Bromobenzenesulfonate[d]	....	57–58	$[\alpha]^{21}_D$ +19.8[c]	$C_{16}H_{17}O_3SBr$	52.03	51.85	4.93	4.66
			B.p., °C. (mm.)						
XIII	2-Phenyl-2-butanol	1.5162	103 (16)	....	....	...	...	...	...
VII	2-Acetoxy-2-phenylbutane	1.4943	.....	....	$C_{12}H_{16}O_2$	74.96	74.94	8.38	8.37
III	*cis*-2-Phenyl-2-butene[e]	1.5402	193	....	....	...	...	...	...
IV	*trans*-2-Phenyl-2-butene[e]	1.5193	173	....	....	...	...	...	...
V	2-Phenyl-1-butene[f]	1.5262	182	....	$C_{10}H_{12}$	90.84	90.72	9.16	9.25
..	(−)-3-Phenyl-1-butanoic acid	....	.....	α^{20}_D −56.5[g,h] $[\alpha]^{25}_D$ −58.5[i,h]	....	...	...	...	...
IX	(−)-3-Phenyl-1-butanol	1.5186	.....	α^{25}_D −39.0[g]	....	...	...	...	...
X	(−)-3-Phenyl-1-bromobutane	1.5350	.....	α^{25}_D −104.3[g]	....	...	...	...	...
XI	(−)-1-N,N-Dimethyl amino-3-phenylbutane	1.4933	.....	$[\alpha]^{22}_D$ −25.8[j]	$C_{12}H_{19}N$	81.29	81.59	10.81	10.81
VI	(−)-3-Phenyl-1-butene	1.5055	.....	$[\alpha]^{22}_D$ −6.39[k]	$C_{10}H_{12}$	90.84	90.82	9.16	9.30
XII	(−)-3-Phenylbutane	1.4878	.....	α^{23}_D −24.3[g,l]	....	...	...	...	...

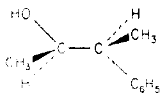
[a] Prepared from alcohol IA, $[\alpha]^{23}_D$ +32.1°. [b] The compound seemed to solidify and remelt at 77–78°. [c] Benzene solution, $c \cong 5\%$. [d] Prepared from alcohol IIB, $[\alpha]^{23}_D$ −0.51°. [e] Compounds have been previously reported (ref. 1) but more highly purified samples are reported here. The densities of these substances were erroneously reported (the *MR*D's were correct) in Paper IV of this series (ref. 3). Correct values are: *cis*-2-phenyl-2-butene, d^{25}_4 0.9191: *trans*-2-phenyl-2-butene, d^{25}_4 0.8918. [f] d^{25}_4 0.8984, MR_D 45.18. [g] Pure liquid, l = 1 dm. [h] T. D. Stewart and D. Lipkin (ref. 5) reported $[\alpha]^{25}_D$ −47.92° (pure liquid); P. A. Levene and R. E. Marker (ref. 22) reported α^{25}_D −52.8° (l = 1 dm., pure liquid); H. Rupe (ref. 5) reported $[\alpha]^{20}_D$ −57.23° (benzene, c = 9%). [i] Benzene, c = 3%. [j] d^{25}_4 0.8861, rotation taken on pure liquid. [k] d^{22}_D 0.8809, d^{25}_4 = 0.8792, MR_D = 44.63. [l] J. Kenyon, *et al.* (ref. 8), reported α^{20}_D +23.6° (l = 1 dm.) for this hydrocarbon.



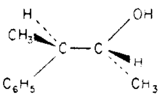
comparison of the relative abilities of phenyl, methyl and hydrogen to participate in an intramolecular displacement reaction can be made. The importance of steric effects in the transition states leading to rearranged products and to conjugated olefins can be assessed through a comparison of their geometry and the corresponding product balances. Finally, this system allows a number of concurrent reactions to be brought under observation at the same time with the end in view of distinguishing which reactions have common intermediates and which do not.



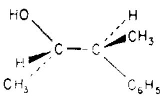
IA
$[\alpha]^{25}_D$ +30.9°



IB
$[\alpha]^{25}_D$ −30.2°



IIA
$[\alpha]^{25}_D$ +0.68°



IIB
$[\alpha]^{25}_D$ −0.69°

Methods and Results

The physical properties and analyses of the starting materials and products are reported in Table I of this paper, and in Table I of the preceding paper of this series.[1] The numbering system for the various isomers of 3-phenyl-2-butanol which has been previously adopted[1,3] has been maintained here.

The conditions for the solvolyses in acetic acid of the *p*-toluenesulfonates and *p*-bromobenzenesulfonates of IA, IB, IIA and IIB are reported in Paper V of this series,[1] as well as the conditions for the decomposition of these esters in acetonitrile. The results of the analyses of the acetates of the secondary alcohols produced in the acetolysis experiments as well as changes that occur in the starting ester prior to solvolysis are also reported in Paper V.[1] Furthermore, the methods of separating starting material, olefin and the oxygen-containing products of solvolysis (through chromatography) were elaborated.[1]

Highly purified samples of the four 2-phenylbutenes were prepared for use as standards for the infrared analysis scheme. The isomeric *cis*- and *trans*-2-phenyl-2-butenes (III and IV) have been previously reported.[3] The preparation of 2-phenyl-1-butene (V) was accomplished through the lithium aluminum hydride reduction of 2-phenylbutanoic acid to 2-phenyl-1-butanol, with subsequent dehydration (the olefin was distilled from a hot mixture of alcohol and solid potassium hydroxide) according to the method of Sabetay.[4] Optically pure (−)-3-phenyl-1-butene (VI) was prepared in the following fashion. Optically pure (−)-3-phenyl-1-butanoic acid was reduced to

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(3) D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

(4) S. Sabetay, *Bull. soc. chim.*, [4] **47**, 614 (1930).

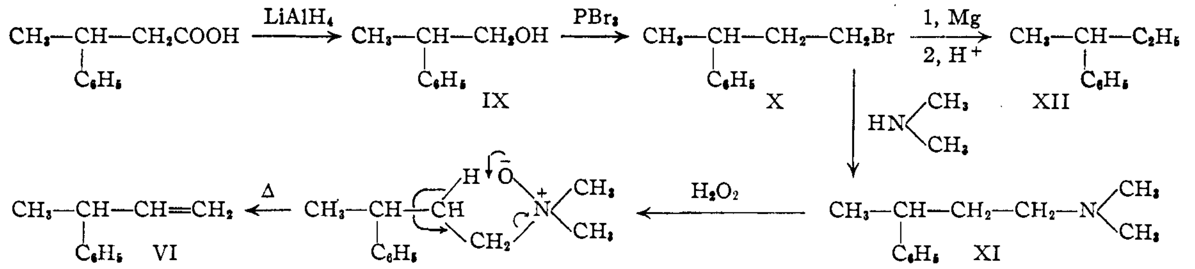
TABLE II

OPTICAL DENSITIES OF THE FOUR PURE 2-PHENYLBUTENES AND TWO SAMPLE MIXTURES AT WAVE LENGTHS IN THE INFRARED EMPLOYED FOR ANALYSIS

Composition of olefinic starting materials in %				Optical density[a]					
				Slit width = 0.92 mm.		Slit width = 2.82 mm.			
III	IV	V	VI	pin 8 $\lambda = 10.09\mu$	pin 10 $\lambda = 12.02\mu$	pin 9 $\lambda = 11.05\mu$	pin 11 $\lambda = 12.25\mu$	pin 12 $\lambda = 12.91\mu$	pin 13 $\lambda = 14.00\mu$
100	0	0	0	0.390	0.957	0.203	0.237	0.178	0.301
0	100	0	0	.120	.380	.422	1.015	0.322	.521
0	0	100	0	.166	.130	.641	0.054	1.310	.988
0	0	0	100	1.100	.105	1.070	.034	0.612	.479
Olefin from run 18				0.301	.464	0.628	.710	.613	.558
23.4	55.6	9.04	11.9	.315	.462	.630	.718	.561	.540
Olefin from run 19				.450	.640	.631	.340	.584	.487
56.4	14.8	11.5	17.2	.463	.628	.660	.354	.569	.485

[a] Values were taken on a Beckman infrared spectrophotometer, Model IR2. In each case a film of 0.03 mm. thickness of the pure olefin was used. The pure olefins, the known mixtures and the unknowns were all run in the same cell within five hours of one another. A glass shutter and NaCl cells were employed.

(−)-3-phenyl-1-butanol (IX) which was converted through the bromide X to (−)-1-N,N-dimethylamino-3-phenylbutane (XI) which was oxidized to the corresponding amine oxide.[5] Pyrolysis of this substance according to the elegant method of Cope[6] gave a good yield of VI without any accompanying isomerization to the conjugated 2-phenylbutenes taking place.[7] The optical purity of the compounds involved in the reaction sequence was demonstrated by the conversion of bromide X to optically pure (−)-3-phenylbutane (XII).[8]



making use of the fact that III and IV produce acetophenone, and V, propiophenone on ozonolysis. Figure 2 records a plot of percentage composition of known mixtures of acetophenone and propiophenone against the optical density at the three wave lengths in the infrared that are the most advantageous for analysis. After the unknown mixtures of olefin were submitted to ozonolysis, the aldehydes were removed through the use of silver oxide, and the mixtures of acetophenone and propiophenone were submitted to infrared analysis. Table IV reports the results of these analyses along with the results that would be predicted from the infrared analysis of the mixtures of the olefins themselves.

Figure 1 records the infrared spectra of the four isomeric 2-phenylbutenes, and enough points of difference are present in the spectra to permit quantitative analysis of four component mixtures of these olefins. Table II records the optical densities of each of the four olefins at the six wave lengths used for the analysis. The large differences in the intensities of absorption allow the analyses to be made with an accuracy of about ±1%. The unknown mixtures in each case were corrected to known mixtures for deviations from Beer's law (Table II reports two sample analyses). In Table III is recorded the conditions of each experiment and the final values for the analyses of the unknown mixtures.

A second and independent check on the general validity of the method of analysis was developed

The amounts of optically active 3-phenyl-1-butene (VI) in the olefinic mixtures from the solvolyses were first estimated from the rotations of the mixtures and from that of optically pure 3-phenyl-1-butene. Making use of this estimate and the infrared analytical data, synthetic mixtures of olefins were prepared utilizing optically active 3-phenyl-1-butene. The rotations of these mixtures confirmed the estimates of optically pure VI among the olefinic products of the reaction. Table III records the results.

The control experiments (see Table V) prove that the olefins once formed are stable under the conditions of the various experiments, and that the isolation procedures are non-selective in manipulative losses. Furthermore, no acetate was formed from olefin under any of the experimental conditions.

To determine the ratios of olefinic products produced by the loss of a proton from the methyl ethyl phenyl carbonium ion, 2-acetoxy-2-phenylbutane was completely decomposed to olefin at 75° in glacial acetic acid. The product balance was

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[5] The acid was prepared according to the method of T. D. Stewart and D. Lipkin [THIS JOURNAL, **61**, 3295 (1939)] and resolved by the method of H. Rupe [*Ann.*, **369**, 323 (190)9].

[6] A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

[7] The pyrolysis of amine oxides (at relatively low temperatures) to give olefins (ref. 6) probably represents another case (analogous to the Chugaev reaction) of a *cis*-elimination reaction (ref. 3), the strongly nucleophilic oxygen of the amine oxide pulling the proton from the adjacent methylene group in a completely concerted reaction.

[8] P. W. Harrison, J. Kenyon and J. R. Shephard, *J. Chem. Soc.*, 658 (1926).

TABLE III

ANALYSES OF OLEFINIC PRODUCTS OF SOLVOLYSIS[a]

Run no.	Config. sta. mat.[b]	Sol.[c]	T, °C.	Hr.	Yld., ol.,[d] %	Yld., alc.,[d] %	Opt. pure 3-phenyl-1-butene in olef. mixture,[e] %	Composition of olefinic mixtures by infrared analyses[f] % III pins 8, 10 11, 13	% III pins 9, 10 11, 12	% IV pins 8, 10 11, 13	% IV pins 9, 10 11, 12	% V pins 8, 10 11, 13	% V pins 9, 10 11, 12	% VI pins 8, 10 11, 13	% VI pins 9, 10 11, 12	Totals pins 8, 10 11, 13	Totals pins 9, 10 11, 12
3	IA	Gl. ac.	75	33	35	53	1.3	42	41	28	29	24	24	6.7	6.2	100	100
4	IB	Gl. ac.	75	33	35	53	1.9	44	44	26	26	22	23	9.5	7.8	101	101
5	IIA	Gl. ac.	75	33	23	68	13	56	56	8.0	8.2	24	23	14	13	101	100
6	IIB	Gl. ac.	75	33	22	69	14	58	58	5.7	6.2	24	22	15	14	102	100
12	IB	Actnit.	82	67	67	0	..	34	35	33	34	10.3	8.6	23	23	101	100
13	IIA	Actnit.	82	67	50	0	..	45	45	21	23	13	11	21	21	100	100
18	IA	Gl. ac.	30	256	12	70	..	24	24	55	54	13	13	10	10	102	101
18A[g]	IA	Gl. ac.	..	256	31	54	..	40	40	27	27	28	28	5	4	100	99
19	IIB	Gl. ac.	30	256	6	74	..	59	59	13	13	13	14	15	15	100	101
19A[g]	IIB	Gl. ac.	..	256	14	67	..	54	55	7	7	32	32	7	6	100	100

[a] With the exception of runs 18, 18A, 19 and 19A, the compositions of the alcoholic products and recovered starting materials are reported in Table II, Paper V of this series (ref. 1). The run numbers are carried over into this investigation. [b] The *p*-toluenesulfonate derivatives of the alcohols were the starting materials in all of the runs except 18, 18A, 19 and 19A, in which *p*-bromobenzenesulfonates were utilized. [c] In all the cases where glacial acetic acid (dry) was the solvent, enough NaOAc was present to neutralize the acid liberated. In the runs where acetonitrile was used as solvent, solid K_2CO_3 was present as a second phase. [d] These yields were calculated on the basis of the amounts of sulfonate ester consumed rather than on the amounts initially used. In runs 3–6, all of the starting material was consumed. [e] Values calculated from rotations of olefinic mixtures as compared to rotations of known mixtures. [f] See Table II for the conditions under which analyses were made, and the correlation between pin numbers and the wave lengths. [g] See section on Methods for explanation of these runs.

only slightly effected by the presence of acetate ion in the reaction mixture (Table V) and was entirely different than the balance found under equilibrating conditions.[9]

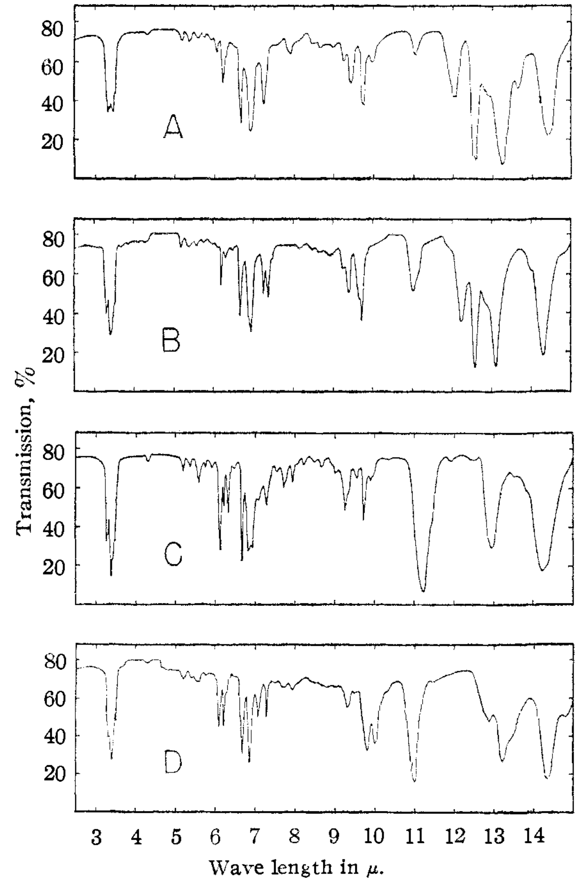

Fig. 1.—Infrared spectra: Baird spectrograph with NaCl prism, liquid film, 0.01 mm. thickness: A, *cis*-2-phenyl-2-butene (III); B, *trans*-2-phenyl-2-butene; C, 2-phenyl-1-butene (V); D, 3-phenyl-1-butene (VI).

Besides analyzing the olefinic mixtures, it was desirable to analyze for 2-acetoxy-2-phenylbutane (VII) in the acetate portion of the acetolysis products. Paper V[1] reported that when the acetolyses of the *p*-toluenesulfonates of IA and IIA were conducted at 75° in acetic acid (runs 3–6)

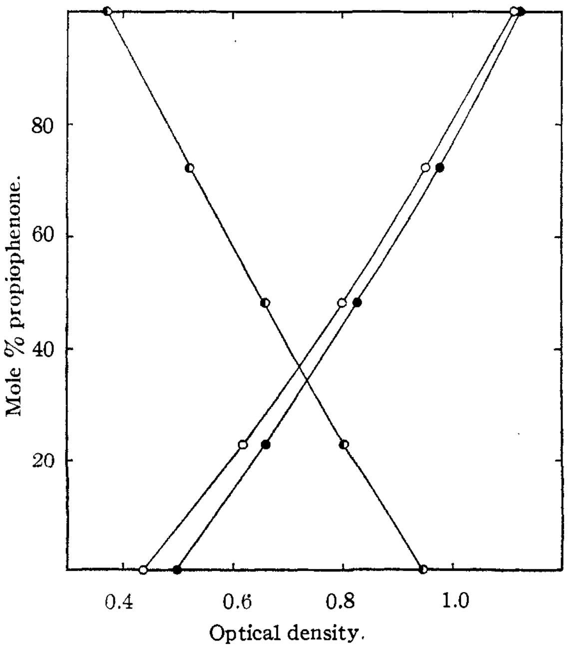

Fig. 2.—Optical densities of mixtures of acetophenone and propiophenone at three wave lengths in the infrared: $\lambda = 9.97\,\mu$ (●); $\lambda = 10.70\,\mu$ (○); $\lambda = 1.295\,\mu$ (◐). Determined with Beckman model IR2 spectrophotometer; NaCl prism; slit width = 0.92 mm.; liquid films of 0.03 mm. thickness.

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(9) Unpublished results.

TABLE IV

INFRARED ANALYSES OF MIXTURES OF ACETOPHENONE AND PROPIOPHENONE OBTAINED BY OZONOLYSIS OF OLEFINIC MIXTURES[a]

Ketonic mix. from oz. of ol.[b]	Mole % acetophenone[c] λ = 9.97 μ	λ = 10.70 μ	λ = 12.95 μ	Mole % propiophenone[c] λ = 9.97 μ	λ = 10.70 μ	λ = 12.95 μ	Mole % propiophenone[d] predicted
Run 4	77	78	80	23	22	20	24
Synth. mixt.[e]	74	77	77	26	23	23	25
2-Phenyl-1-butene	0	2	0	97	98	97	100

[a] Run on a Beckman infrared spectrophotometer, Model IR2, fitted with a turret accessory. All analyses and standards were run in the same cell (NaCl-prisms) on undiluted liquid films of 0.03 mm. thickness (slit = 0.92 mm.). [b] The aldehydic products of the ozonolysis were removed (see experimental). [c] Values were obtained by reading the percentages from the plot of optical density *vs.* concn. (Fig. 2). [d] Predictions are made on the assumption that the yield of 2-phenyl-1-butene → propiophenone is equal to the yield of 2-phenyl-2-butene → acetophenone. [e] Composition: III, 42.3%; IV, 25.4%; V 22.6%; VI, 9.8%.

no tertiary acetate was produced. When the same reaction was conducted at 30° (runs 18 and 19, Table IV), considerable amounts of the substance were detected by the following means. Although tertiary acetate VII goes completely to olefin at 75° but survives at 30° in glacial acetic (runs 24, 25 and 26 of Table V), the acetates of I and II are preserved under both sets of conditions.[1] Therefore the olefin–acetate mixtures obtained from the acetolyses run at 30° (runs 18 and 19) were each divided into two parts, and one part was rid of tertiary acetate by treatment with acetic acid at 75° (runs 18A and 19A). The two parts were each converted to olefin-free alcoholic mixtures which were submitted to infrared analysis. The mixtures that contained tertiary alcohol were treated like a two component system with tertiary alcohol as one component and secondary alcohol (I and II) as the other. Table VI reports the optical densities in the infrared of the following: pure 2-phenyl-2-butanol; the secondary alcohol mixtures of runs 18A and 19A; the secondary–tertiary alcohol mixtures; and two synthetic mixtures prepared from 2-phenyl-2-butanol and the secondary alcohols obtained in runs 18A and 19A.[10] Three independent sets of two simultaneous equations in two unknowns were solved, and the values obtained for each component were corrected to the known mixtures for deviations from Beer's law. The results are tabulated in Table VII.

TABLE V

CONTROL EXPERIMENTS FOR OLEFINIC PRODUCTS OF SOLVOLYSIS

Run no.	Composition of olef. starting materials % III	% IV	% V	% VI	Solvent[b]	Moles[c] base add.	Time, hr.	Temp., °C.	% Ol. rec.	Composition of olefinic mixture by infrared analysis[a] % III 8, 10 11, 13	% III 9, 10 11, 12	% IV 8, 10 11, 13	% IV 9,10 11, 12	% V 8, 10 11, 13	% V 9, 10 11, 12	% VI 8, 10 11, 13	% VI 9, 10 11, 12	Totals 8, 10 11, 13	Totals 9, 10 11, 12
20[d]	42.3	25.4	22.6	9.7	Gl. acet.	0.2	33	75	83	43	43	28	28	18	21	9.4	8.1	99	100
21[d]	55.9	7.3	22.6	14.2	Gl. acet.	0.2	33	75	77	58	58	8	8	19	20	13	12	98	98
22[e]	0	0	100	0	Acetonit.	3.5	39	82	93	4.5	3.5	8.5	8	85	86	4	4	102	102
23[d,f]	30	35	17	18	Gl. acet.	8.9[h]	144	30	82	...	...	...	..	..	..	..	..	...	...
24	2-Acetoxy-2-phenylbutane				Gl. acet.	0	26	75	81	52	52	2	1.5	46	47	0	0	100	101
25					Gl. acet.	1.0	26	75	90	55	55	4	2	42	45	0	0	101	102
26[g]					Gl. acet.	6.7[h]	192	30	4	..	..	..	..	..	..	..	..	...	...

[a] These analyses were made on the same spectrophotometer using the same techniques as those reported in Tables II and III. [b] Solutions were made free of water by addition of excess acetic anhydride. [c] Starting material = 1 mole. [d] Mixtures made up gravimetrically from pure olefins. [e] *p*-Toluenesulfonate of I (0.95 mole, starting ol. = 1 mole) was added, solid K_2CO_3 was present as a second phase. [f] No alcohol could be isolated after the mixture had been reduced with $LiAlH_4$. [g] The acetate was optically active. After reduction with $LiAlH_4$, a 71% yield of alcohol was recovered, retaining 78% of its initial activity. [h] The concentrations of acetate ion were about equivalent to the average concentration found in runs 18 and 19 (See Table III).

TABLE VI

OPTICAL DENSITIES OF 2-PHENYL-2-BUTANOL AND 3-PHENYL-2-BUTANOL SAMPLES AT THE WAVE LENGTHS USED FOR ANALYSIS IN THE INFRARED[a]

	Optical densities of a solvent-free 0.03 mm. liq. film; Slit width = 0.92 mm.[b] λ = 8.10 μ pin 6	λ = 8.30 μ pin 7	λ = 8.60 μ pin 8	λ = 10.38 μ pin 9	Slit width = 0.82 mm.[c] λ = 11.67 μ pin 10	λ = 13.46 μ pin 13	λ = 13.62 μ pin 14
2-Phenyl-2-butanol	0.548	0.820	1.210	0.283	0.741	0.354	0.305
Alc. from 18	.927	.468	0.589	.478	.328	.810	.659
Alc. from 18A[d]	.999	.365	.304	.530	.159	.950	.772
Alc. from 19	.758	.395	.475	.825	.214	.560	.647
Alc. from 19A[d]	.730	.336	.348	.890	.156	.602	.702
25% tert. 75% alc. 18A[d]	.904	.492	.627	.472	.310	.819	.667
12% tert. 88% alc. 19A[d]	.712	.406	.490	.828	.231	.588	.669

[a] Beckman infrared spectrophotometer, Model IR2, with a turret accessory was employed. The standards and unknown samples were run in the same cell, the readings being taken within an hour of each other. NaCl cells were used. [b] A metal shutter was used. [c] A glass shutter was used. [d] In these samples the acetate of 2-phenyl-2-butanol was removed by decomposition in dry acetic acid at 75° from aliquot samples of the acetate–olefin mixtures obtained in runs 18 and 19.

The tertiary alcohol of run 19 was demonstrated to be completely racemic through the equivalence of the rotations of the alcohol mixture from run 19, and a synthetic model prepared from racemic 2-phenyl-2-butanol and the secondary alcohol from run 19A. To establish the fact that optically active tertiary acetate (VII), had it once been

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(10) The complete infrared spectra of the two diastereomeric 3-phenyl-2-butanols and 2-phenyl-2-butanol are reported in Table V of this series.

TABLE VII

THE ALCOHOLIC PRODUCTS OBTAINED BY REDUCTION OF THE ACETATE MIXTURES FROM THE SOLVOLYSES AT 30° IN GLACIAL ACETIC ACID

Run no.	Start. config. bros.	Mat. wt. g.	Yld. alc., %	α^{21}D[a] alc.	Anal. of alc. mixt. by infrared[b]									Recovered sulfonate ester[c]					
					% tert. at pins			% sec. at pins			total % at pins			1st crop			2nd crop		
					6+ 10	8+ 14	7+ 13	6+ 10	8+ 14	7+ 13	6+ 10	8+ 14	7+ 13	Yld., %	M.p., °C.	$[\alpha]^{21}$D[d]	Yld., %	M.p., °C.	$[\alpha]^{21}$D[d]
18	IA	50	33	+0.47°	21	23	23	79	76	75	100	99	98	49	92–94[e]	+ 2.2°	3.5	76–78[f]	+20.2
18A	IA	..	28	+0.52	..	..	..	..	..	..	...	..	..	..	....	.....	...	.....	.....
					% tert. at pins			% sec. at pins			total % at pins								
					7+ 9	8+ 14	10+ 13	7+ 9	8+ 14	10+ 13	7+ 9	8+ 14	10+ 13						
19	IIB	50	42	−2.36	11	12	11	88	85	85	99	97	96	39	57–58[g]	+20.1	2.7	57–58[g]	+19.4
19A	IIB	..	38	−2.14	..	..	..	..	..	..	...	..	..	..	....	.....	...	.....	.....

[a] Observed rotation on liquid sample, l = 1 dm. [b] See Table VI for correlation between pin numbers and wave lengths employed, and for the slit widths at the given wave lengths. In each case the analyses are corrected to standards not more than 3% away in composition. [c] In run 18, a residue of 0.8%, and in run 19, a residue of 0.7% was obtained by concentrating the combined filtrates from these crystallizations. [d] Benzene, $c \cong 5\%$. [e] M.m.p. with authentic I *p*-bromobenzenesulfonate, 93–94°. [f] M.m.p. with authentic IA *p*-bromobenzenesulfonate, 76–78°. [g] M.m.p. with authentic IIB *p*-bromobenzenesulfonate, 57–58°.

formed in run 19 could have preserved its activity, a sample of optically active VII[11] was submitted to the conditions of experiment 19. Only 23% of the original activity of the tertiary acetate was lost.[12]

Discussion

It has been established through kinetic studies[13] that the appearance of *p*-toluenesulfonic acid in the acetolysis of the *p*-toluenesulfonate esters of I and II is a first order process, and that neither the order nor rate are affected (outside the range of salt effects) by changing the concentration of acetate ion present in the reaction mixture. This fact coupled with the absence of acetate products that could have arisen from an S_N2 reaction[1] provides evidence that the olefins produced during the acetolysis reaction arose by an E_1 mechanism.[14] The absence of base in the acetonitrile solution used in runs 12 and 13 makes the production of olefin appear to have also occurred by the E_1 mechanism.

Reaction Paths for the E_1 Reaction.—From the structural and stereochemical relationships between starting materials and products, it is apparent that a number of different reaction paths are needed to account for the results.

Path A IA or IIA Tos. $\longrightarrow$ phenonium ion $\longrightarrow$ I or IIA acetate

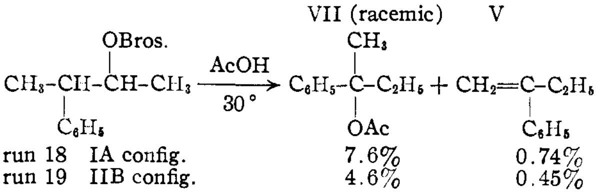
Path B IA or IIA Tos. $\xrightarrow{S_N1}$ IA and IIA acetate

Path C IA or IIA Tos. $\xrightarrow[\text{migration}]{\text{H}}$ III + IV + V + VII (racemic)

Path D IA or IIA Tos. $\xrightarrow[E_1\text{ reaction}]{\text{non-stereospecific}}$ VI (active) + III + IV

Path E IA or IIA Tos. $\xrightarrow[\text{reaction}]{trans\ E_1}$ IV or III

The existence of paths A and B has been demonstrated previously.[1] Evidence for Path C is found in the results of the acetolysis experiments. The data indicate that a common intermediate is the precursor of both the inactive tertiary ester (VII) and the structurally related 2-phenyl-1-butene (V), and that this intermediate is produced from members of both racemate series. Thus in glacial acetic acid at 30° both IA and IIB *p*-bromobenzenesulfonates gave VII and V in the ratio of ten to one despite the fact that the absolute amounts of the two products varied by almost a factor of two.[15] The completely racemic character of the tertiary acetate obtained indicates that the intermediate is symmetrical,[16] and the nature of the products suggests that this intermediate is the methylethylphenylcarbonium ion.



VII (racemic) V

$$\underset{\text{C}_6\text{H}_5}{\text{CH}_3\text{–CH}}\text{–}\overset{\text{OBros.}}{\text{CH}}\text{–CH}_3 \xrightarrow[30°]{\text{AcOH}} \text{C}_6\text{H}_5\text{–}\underset{\text{OAc}}{\overset{\text{CH}_3}{\text{C}}}\text{–C}_2\text{H}_5 + \text{CH}_2\text{=}\underset{\text{C}_6\text{H}_5}{\text{C}}\text{–C}_2\text{H}_5$$

run 18 IA config. 7.6% 0.74%
run 19 IIB config. 4.6% 0.45%

At 75° in acetic acid the ionization of VII[17] produced a mixture of III, IV and V, and since this reaction probably also goes by way of the methylethylphenylcarbonium ion, it is likely that olefins III and IV as well as V were produced by path C. Evidence for this contention is found in the relationship of the degree of stereospecificity for the reaction giving III and IV and the amount of rearranged olefin (V) formed. At 75° in acetic acid (runs 3 and 5) where the amount of V is relatively high, the degree of stereospecificity is low. At 30° in acetic acid (runs 18 and 19) where the amount of V is relatively low, the degree of stereospecificity is high.

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(11) The author wishes to express his appreciation to H. Zeiss [see THIS JOURNAL, **73**, 2391 (1951)] for a sample of (−)-2-phenyl-2-butanol.

(12) M. P. Balfe, G. H. Beaven and J. Kenyon [*J. Chem. Soc.*, 376 (1951)] have shown that the acetate of optically active phenylcyclohexylcarbinol racemizes slowly in acetic acid at 100°.

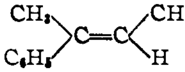
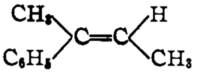
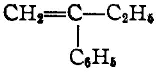
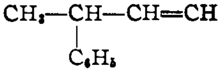
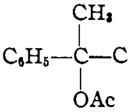
(13) S. Winstein, *et al.*, THIS JOURNAL, **74**, 1127 (1952).

(14) M. L. Dhar, E. D. Hughes and C. K. Ingold [*J. Chem. Soc.*, 2062 (1948)] have pointed out that when the basicity of the nucleophilic reagent is progressively diminished, its power to attack hydrogen and thereby produce a bimolecular elimination reaction disappears much more rapidly than its power to attack carbon.

(15) Although other rearrangements occur concurrently (*e.g.*, IIA Bros. → IIA Bros. in run 19) the stereochemical identity of the starting material is preserved.

(16) H. Zeiss has reported [Abstract of Papers Presented Before the Division of Organic Chemistry at the Meeting of the American Chemical Society, Chicago, Ill. (1950)] that the solvolysis in boiling methanol of (−)-hydrogen 2-phenylbutyl-2-phthalate leads to methyl ether which is 88% racemized and 12% active (the asymmetric carbon atom was inverted). In the present work, (−)-2-acetoxy-2-phenylbutane when allowed to stand in glacial acetic acid in the presence of acetate ion at 30° had racemized 23% after 192 hours.

(17) This tertiary acetate is stable at higher temperatures in non-acidic solvents of lower ionizing power such as acetonitrile, and therefore the production of olefin from VII is not a thermal decomposition.

	 III, %	 IV, %	 $CH_2{=}\underset{C_6H_5}{C}{-}C_2H_5$ V, %	 $CH_3{-}\underset{C_6H_5}{CH}{-}CH{=}CH_2$ VI, %
(run 3) IA Tos. $\xrightarrow[75^\circ]{AcOH}$	41	29	24	6.5
(run 5) IIA Tos. $\xrightarrow[75^\circ]{AcOH}$	56	8	23	13
(run 18) IA Bros. $\xrightarrow[30^\circ]{AcOH}$	24	54	13	10
(run 19) IIB Bros. $\xrightarrow[30^\circ]{AcOH}$	59	13	13	15
(run 18A) IA Bros. $\xrightarrow[(1)30^\circ\ (2)75^\circ]{AcOH}$	40	27	28	5
(run 19A) IIB Bros. $\xrightarrow[(1)30^\circ\ (2)75^\circ]{AcOH}$	54	7	32	7
(run 24)  $C_6H_5{-}\overset{CH_3}{\underset{OAc}{C}}{-}C_2H_5$ $\xrightarrow[75^\circ]{AcOH}$	54	3	43	0

The problem now arises as to how much III and IV came from tertiary acetate and related ions in those experiments conducted at 75°. Since the methylethylphenylcarbonium ion is the only source of V in those runs conducted at 30°, a similar situation probably exists at 75°. Therefore, since runs 3, 5 and 24 all produced this tertiary carbonium ion, the amounts of V in runs 3 and 5 can be used to measure the amounts of III and IV produced by path C.

III	IV	V		(run 3)		III	IV	VI
31%	2%	24%	$\xleftarrow[C]{path}$	IA Tos.	$\xrightarrow[D+E]{paths}$	10%	27%	6.5%
29%	2%	23%	$\xleftarrow[C]{path}$	(run 5) IIA Tos.	$\xrightarrow[D+E]{paths}$	27%	6%	13%

Since olefins III and IV are produced both stereospecifically and non-stereospecifically by routes other than path C, it seems probable that the non-stereospecific route (D) involves an intermediate that can arise from starting material of either the IA or IIA configuration, such as a methyl-1-phenylethylcarbonium ion. Such an intermediate would be expected to collapse to give not only III and IV but also VI. If VI arises only from this intermediate,[18] then the ratios of VI to those parts of III and IV produced by path D should be the same in runs 3 and 5. Since the ratios of VI to III for run 3 and of VI to IV for run 5 are known, the amounts of IV for run 3 and III for run 5 produced by path D can be calculated. Finally, the amount of IV produced from IA Tos. (run 3) and III from IIA Tos. (run 5) through a *trans* elimination reaction (path E) can be calculated.

			(run 3)		III	IV	V
24%	IV	$\xleftarrow[E]{path}$	IA Tos.	$\xrightarrow[D]{path}$	10%	3%	6.5%
7%	III	$\xleftarrow[E]{path}$	(run 5) IIA Tos.	$\xrightarrow[D]{path}$	20%	6%	13%

Although the total yield of olefin is higher in run 3 than in run 5, the absolute yields of VI in the two runs are reversed. Furthermore, the amount of secondary acetate belonging to the I racemate series which was produced by path B is higher in run 5 than in run 3. Since paths B and D are both non-stereospecific, the possibility that both processes have a common intermediate can be tested by comparing the ratios of VI to I–IA acetate (produced by path B) in runs 3 and 5. The proximity of the ratios suggests that a common intermediate such as the methyl-1-phenylethylcarbonium ion does exist, but since the ratios are not identical, all of the assumptions involved in the calculations cannot be quantitatively correct. For instance, the disparity between the ratios could be explained by a small amount of IIA Tos. producing IA acetate by a one stage bimolecular substitution reaction involving a molecule of solvent.

	% VI	I-IA Acet. by path B, %	VI/I-IA Acet.
(run 3) IA Tos.	2.3	1.6	1.4
(run 5) IIA Tos.	3.0	2.7	1.1

Since these calculations involve a large number of experimental observations, and in some cases errors could accumulate, only qualitative conclusions can be drawn from many of the results. However, that at least three reaction paths must be available for the E₁ reaction has been established. Although analogous calculations cannot be applied to the results of runs 12, 13, 18 and 19, the data suggest that the picture is essentially the same regardless of temperature (30 or 75° in acetic acid) or solvent (acetic acid or acetonitrile).

Mechanisms for the E₁ Reaction.—The great variety of mechanisms available for the simple S_N1 and E₁ reactions as well as for those substitution and elimination reactions that involve Wag-

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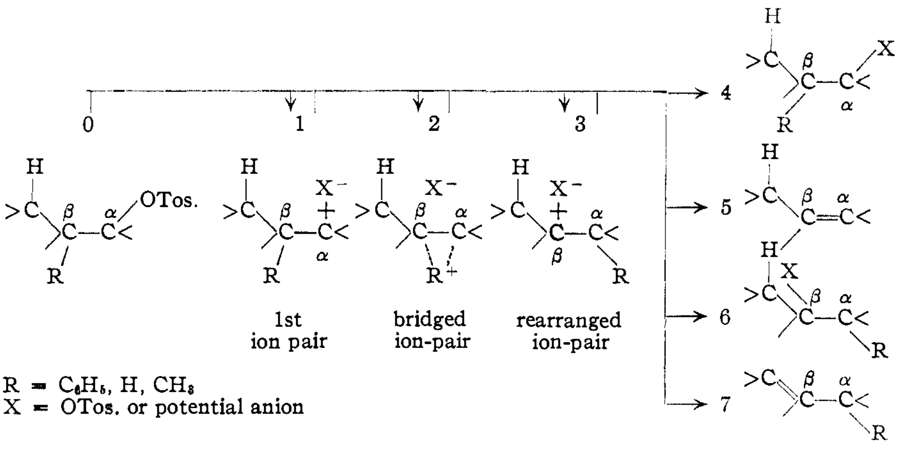
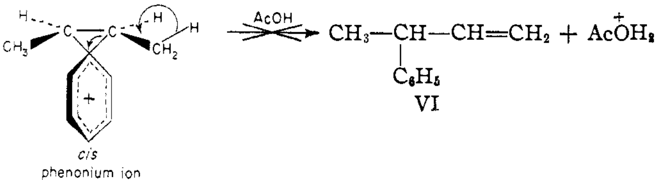
[18] Evidence against two other possible routes will be presented later. Even if part of VI was produced from IA Tos. and IIA Tos. by a path analogous to the stereospecific path E, as long as the relative amounts coming from each starting material were somewhere near equal, the above calculations would have validity.

ner–Meerwein rearrangements are summarized in the diagram. Each of the three ion-pairs represent distinct intermediate stages in the sequence, and along with the starting material and products are designated by digits. A particular mechanism will be referred to in terms of an appropriate combination of digits and dashes, each dash standing for a transition state. The bridged ion-pair in which R = H[19] would probably be capable of maintaining configuration at both the α- and β-carbon atoms in a manner analogous to the case where R = C_6H_5.[1] The first and rearranged ion-pairs might or might not be capable of maintaining asymmetry at the α- or β-carbon atoms, respectively, depending on the degree of solvation, the ionizing power of the solvent and the ability of the substituents attached to the carbonium ion to distribute charge.

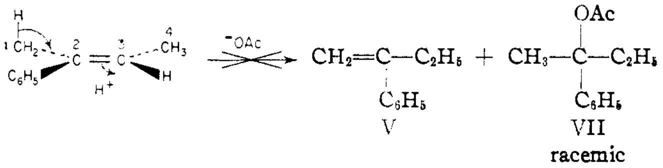


R = C_6H_5, H, CH_3
X = OTos. or potential anion

Evidence that mechanisms involving a 2–7 stage (R = C_6H_5, H) do not operate is found in the results of the acetolysis of IA Tos. at 75° (run 3). In run 3 about 80% of the starting material had become racemic through an isomerization reaction (IA Tos. → I Tos.) before being completely consumed.[1] Therefore the production of VI which is about 80% racemic is consistent with the fact that about 80% of the starting material had become racemic before it went to olefin and acetate products. The agreement between these two percentages excludes any mechanism for the formation of VI which involves an internally compensated intermediate such as the *cis* phenonium ion. The analogous mechanism in which R = H is also improbable on the following grounds. If the hydrogen-bridged ion were to lose a proton from either carbon atoms 1 or 4, certainly the loss from carbon 1 would be favored because of the resonance-stabilized transition state that would be involved.[20] Yet it was demonstrated earlier that V and VII have a common *symmetric* intermediate, a condition that this bridged ion does not fulfill.



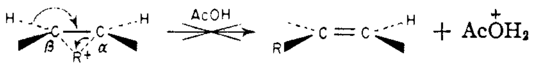
VI



V VII racemic

It also seems improbable that mechanisms can operate in which bridged ions decompose to olefin by the direct loss of a proton from the α- or β-carbon atoms. The geometry of the transition state involved would be such that the electron pair that migrates from the C–H bond to form the C=C bond would have to come in at an angle of considerably less than 180° with reference to the plane of the three-membered ring. Such an angle would probably introduce enough strain into the transition state to make the activation energy for the process prohibitively high.

Olefins III, IV and VI produced non-stereospecifically in runs 3 and 5 through reaction path D probably arise by mechanism 0-1-5 (R = H), the first ion-pair being effectively symmetric at the α-carbon atom. The acetates of I and II that arise through path B probably spring in part from the same intermediate by mechanism 0-1-4.



It has been demonstrated that olefins III, IV and V produced by path C in runs 18 and 19 arise from the same symmetric intermediate that gives rise to the tertiary acetate VII. Therefore mechanisms 0-6, 0-7, 0-1-6, 0-1-7, 0-2-6, 0-2-7, 0-1-2-6 or 0-1-2-7 are inconsistent with either the stereochemistry of the reaction or the existence of a common intermediate for all four products. Mechanisms 0-1-3-6, 0-1-3-7, 0-1-2-3-6, and 0-1-2-3-7 all have the first ion-pair (R = H) as an intermediate. Path D by which VI was probably produced also had the first ion-pair as an intermediate, a species capable of coming from starting material of either the IA or IIA configuration. Should C and D both involve this same ion-pair as an intermediate, and if both VI and V can only arise by paths C and D, respectively, then the ratio of the

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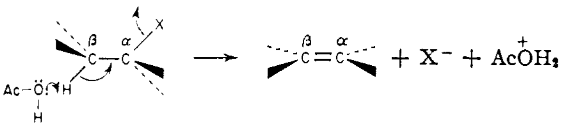
[19] The concept of the protonated double bond was introduced by K. S. Pitzer, This Journal, 67, 1126 (1945). This species has been discussed in connection with organic reaction mechanisms by (a) C. C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 40; (b) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 213; (c) P. D. Bartlett, Twelfth National Organic Chemistry Symposium of the American Chemical Society, June, 1951, Denver, Colorado.

[20] The author is indebted to S. Winstein (private communication) for this point.

yields of VI to V in run 3 (IA Tos.) should equal the ratio of the yields in run 5 (IIA Tos.). The fact that these ratios differ by a factor of two suggests that paths C and D do not have a common stage. Hence mechanisms 0-1-3-6, 0-1-3-7, 0-1-2-3-6 and 0-1-2-3-7 could operate in path D only if the α-carbon was in effect asymmetric in the first ion-pair. A more probable explanation is that the hydrogen on the β-carbon atom participates in the displacement of the sulfonate anion from the α-carbon to give a protonated double bond as an intermediate which then decomposes to a methylethylphenylcarbonium ion as an intermediate, which then goes to III, IV, V and VII (mechanisms 0-2-3-5, 0-2-3-6 and 0-2-3-7). Mechanisms 0-3-5, 0-3-6 and 0-3-7 are also compatible with the facts.

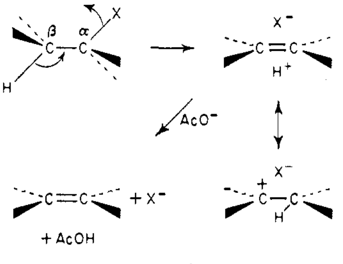
For the stereospecific production of olefin (path E) four mechanisms are available, 0-5, 0-1-5, 0-2-5 and 0-1-2-5 (R = H). Mechanism 0-5 is a bimolecular one-stage process in which a solvent molecule plucks a proton from the β-carbon at the same time that an anion leaves from the α-carbon. In this mechanism, HX could be lost from



the molecule only from that conformation about the $\overset{\beta}{C}$—$\overset{\alpha}{C}$ bond that places the H and X groups *trans* to one another because of the necessity for the pair of electrons initially in the $\overset{\beta}{C}$–H bond to displace X$^-$ from the rear in a Walden inversion type of displacement reaction.[21] The difference between mechanism 0-5 and the conventional E$_2$ mechanism is that the latter reaction is provoked by the attack of a strong base on the $\overset{\beta}{C}$–H bond, the transition state being stabilized by the formation of two new covalent bonds. In the former mechanism the breaking of the $\overset{\alpha}{C}$–X bond to form a stable anion initiates the reaction. The only possible difficulty in applying mechanism 0-5 to the present investigation is that a strong base (AcO$^-$) was present in the reaction mixtures of those runs made in glacial acetic acid, and yet no mechanistic use was made of this base in the rate determining step. This fact suggests, but does not prove, that the breaking of the $\overset{\beta}{C}$–H bond took place after the rate determing step.

Mechanisms 0-1-5 and 0-1-2-5 are consistent with the stereospecificity of path E only if several assumptions are made. The ion-pair involved as an intermediate in these mechanisms would have to be capable of holding configuration at the α-C, and the electron pair initially in the H–$\overset{\beta}{C}$ bond would have to become attached to the α-C only when H and X were *trans* to one another.

In mechanism 0-2-5 (R = H) the reason for the *trans* course of the stereospecific portion of the E$_1$ reaction lies in the necessity for the hydrogen of the β–C becoming bonded at the rear of the α-C, the latter becoming inverted as X$^-$ is displaced. This hydrogen bridge would represent a conjugate acid of a weak base, and like other acids would tend to dissociate, a process that would satisfy the stereochemical requirements of path E.



If mechanism 0-2-5 applies to the stereospecific E$_1$ reaction, the analogy between the formation of a phenyl and hydrogen bridge becomes apparent. Both phenyl and hydrogen would be capable of participating in the displacement of X$^-$ from the α-carbon. Both of these reactions would compete with the non-stereospecific reaction whose mechanism involves simple ionization of the α-C–X bond. Both bridges could collapse to give rearranged products, and both bridges would be responsible for those products that arise by a stereospecific mechanism. Although no evidence for the hydrogen bridge has been presented, attractive and consistent explanations of the data involve this hypothetical intermediate.

The diagram summarizes the mechanisms that are preferred for the reactions that occurred in runs 3 and 5 (glacial acetic acid at 75°). The reaction paths and absolute yields are arranged about the arrows.

The Relative Abilities of Phenyl and Hydrogen to Participate in an Intramolecular Displacement Reaction.—Subject to the reliability of the mechanistic interpretation, the data at hand allow a comparison of the abilities of hydrogen and phenyl to participate in an intramolecular displacement reaction. Since k_a and k_h are first order rate constants, $k_a/k_h = 49/29$. It was demonstrated earlier[1] for run 3 that the rate at which phenonium sulfonate ion-pairs are formed, k_p, is five times the rate at which acetate is formed *via* phenonium ions. Therefore $k_p/k_h = 245/29$; or with IA Tos, the ability of phenyl to participate in an intramolecular displacement reaction is about eight times the ability of hydrogen. Analogous calculations show that the phenyl displaces the sulfonate group in IA Tos about sixty-six times and hydrogen about eight times as often as the sulfonate ester enters into an S$_N$1 reaction with the acetic acid solvent. Due to the stereochemistry of IIA, similar calculations cannot be made for run 5.

49% yield of acetate formed from phenonium sulfonate ion-pairs	$\xleftarrow{k_a}$ IA Tos. $\xrightarrow{k_h}$	29% yield of compounds formed from hydrogen-bridged ions

Since no methyl migration was detected in any of the above reactions, the ability of this group to participate in intramolecular displacement reactions in the 3-phenyl-2-butanol system appears

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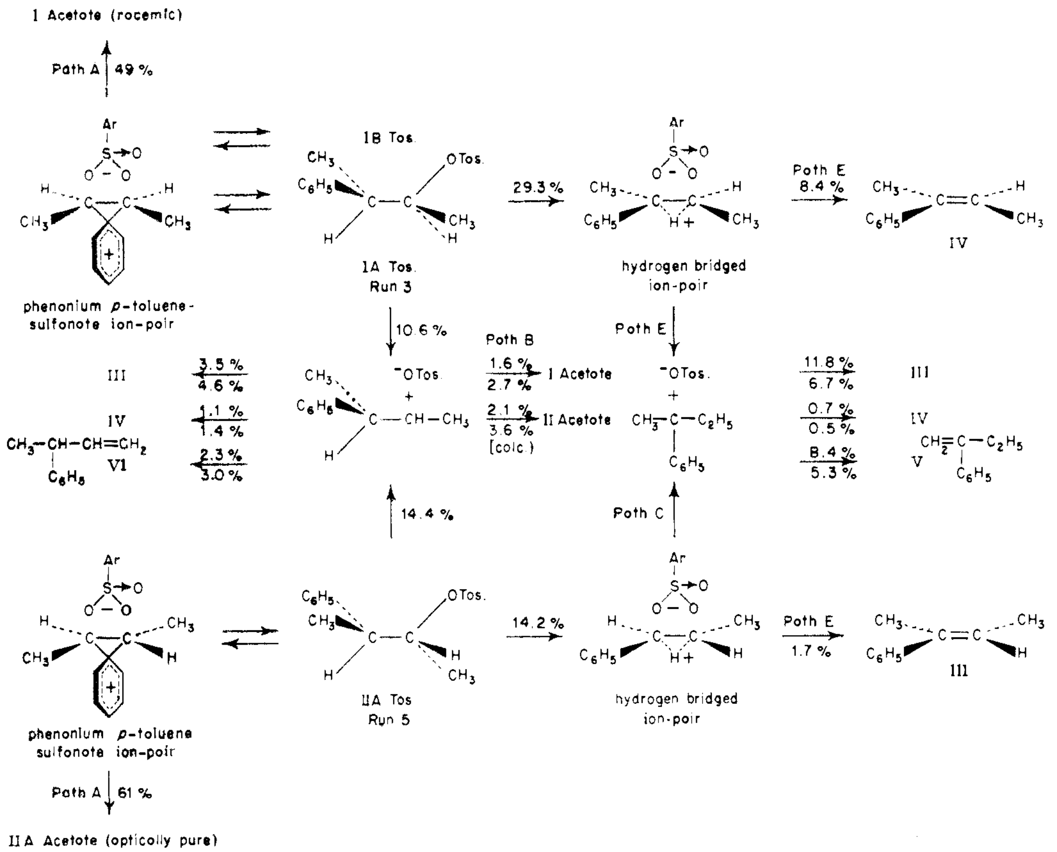
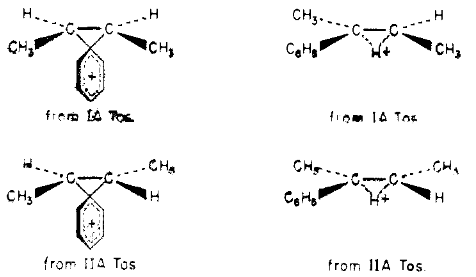
[21] An analogous explanation for the *trans* character of the E^2 reaction has been suggested by both S. Winstein, D. Pressman and W. G. Young (THIS JOURNAL, **61**, 1645 (1939)) and by Ingold, *et al.* [*J. Chem. Soc.*, 2093 (1948)].



to be poor relative to the ability of phenyl and hydrogen.

The factors that must be considered when comparing the abilities of hydrogen and phenyl to participate in an intramolecular displacement reaction are both steric and electronic in character. The phenyl group appears to be somewhat better able to distribute charge and thus stabilize a bridged ion when it is bridging than when it is staying behind. The same is probably even more true of hydrogen. The importance of steric factors is measured by the differences in product balances as one passes from one diastereomeric starting material to another. In the IA system, both the phenyl and hydrogen bridges have bulky groups distributed *cis* to one another. In the IIA system only the hydrogen bridge has two bulky groups distributed *cis* to one another. Since the processes of hydrogen and phenyl bridge formation compete with one another, one would expect that the formation of a phenyl bridge would be less favored over a hydrogen bridge in the IA than in the IIA system. The facts are in accord with this hypothesis. Thus the total yield of olefin is always higher from IA Tos. than from IIA Tos. This difference in total yield of olefin (12%) is entirely accounted for by the difference in yields (15%) of that olefin which arises only by way of the hydrogen bridge (paths C and E).



Finally, the relative weights of hydrogen and phenyl would tend to favor hydrogen-over phenyl-bridge formation since the cost in energy in moving and orienting to a rigid geometry a group of seventy-seven atomic weight units should be more than for a group of little bulk and of one atomic weight unit. Since such a large number of factors control the Wagner–Meerwein rearrangement and elimination reactions, a proper assessment of their relative importance can be gained only by a thorough study of a number of different systems.

Experimental Part

Preparation of (−)-3-Phenyl-1-butene (VI).—The menthol ester of 3-phenylbutyric acid[5] (prepared from 61 g. of acid) was recrystallized three times from ethanol to give white staffs, m.p. 46–47°, $[\alpha]^{23}\text{D} \cong -80.3°$ (*c* 5% benzene). A fourth recrystallization gave material of almost identical rotation ($[\alpha]^{23}\text{D}$ −80.1°). Hydrolysis of the ester[5] produced 13.75 g. of optically pure (−)-3-phenylbutyric acid (see Table I). This material was dripped into a stirred solution of 3.0 g. of lithium aluminum hydride in ether, and the resulting mixture was stirred eight hours and poured into a mixture of ice and 10% sodium hydroxide solution. After the organic layer had been separated and well washed with water it was dried, the ether was evaporated, and the resulting oil was distilled to give 10.6 g. of (−)-3-phenyl-1-butanol[22] (see Table I). This alcohol (10.0 g.) was converted to (−)-3-phenyl-1-bromobutane by the method of

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[22] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **100**, 685 (1933).

Levene,[22] and 12.6 g. of the bromide (see Table I) was obtained. A small sample (1.5 g.) of this bromide was converted to (−)-2-phenylbutane (see Table I) through treatment of the halide first with magnesium and then with acid.[22]

A mixture of 11.0 g. of (−)-3-phenyl-1-bromobutane, 12 g. of dimethylamine and 20 ml. of pure dioxane was heated in a sealed tube at 100° for 12 hours. The tube was then opened and the contents shaken with a mixture of pentane[23] and alkaline solution. The organic layer was thoroughly washed with water, and the amine was extracted into 0.1 *N* hydrochloric acid solution which in turn was washed with pentane. The aqueous solution was made basic, the amine extracted into pentane, the pentane was washed with water and dried. After evaporation of the solvent the residual oil was distilled to give 8.25 g. of (−)-1-N,N-dimethylamino-3-phenylbutane (colorless oil).

The amine (8.0 g.) was converted to its oxide by stirring with 12.0 g. of 30% H_2O_2 at room temperature for 24 hours.[6] The excess hydrogen peroxide was decomposed with an extract of catalase (prepared from avocado skins), the solution was filtered, frozen and the water was removed by sublimation at low pressure. The amine oxide was then heated under 2 mm. of pressure at a temperature of 120° until the decomposition was complete (ten minutes), the mixture of olefin and hydroxylamine that distilled being collected in a Dry Ice trap. This distillate was shaken with a mixture of pentane and water, the pentane layer was washed with dilute acid, dilute base, and finally with water. Removal of the pentane and distillation of the residue produced 4.7 g. of (−)-3-phenyl-1-butene (see Table I). The freedom of this non-conjugated olefin from even small amounts of conjugated olefin is shown by the very low extinction coefficient (ϵ = 56) of the substance at 238 mμ in the ultraviolet absorption spectrum. The extinction coefficient for 2-phenylbutane at the same wave length is 45.[24]

Preparation of the Conjugated 2-Phenylbutenes.—These olefins (III,[3] IV[3] and V[4]) were repeatedly fractionated at a temperature below 100° until the first and last fractions had identical indexes of refraction and gave the same extinction coefficients at the six wave lengths in the infrared that were used for analysis (see Table II). When heated above 100° for long periods of time they slowly isomerize to VI.

Solvolyses in Glacial Acetic Acid.—The conditions under which runs 3–6 were carried out as well as the procedures for separating both alcohol and olefin fractions are reported in Paper V of this series.[1] The olefinic mixture was isolated from the chromatogram filtrates by evaporation of the pentane through a short column and flash-distillation (at 20 mm. pressure) of the residual oil. At no point was the olefinic mixture heated higher than 100°. This distillate was used directly for the analyses.

In runs 3–6 the amounts of optically pure 3-phenyl-1-butene were determined through the rotations of the liquid samples (in run 3, α^{23}_{D} +0.073°; in run 4, α^{23}_{D} −0.107°; in run 5, α^{23}_{D} +0.744°; in run 6, α^{23}_{D} −0.794°, l = 1 dm. for all runs). As a model for runs 3 and 4, a synthetic mixture of the following composition was prepared: III, 41%; IV, 29%; V, 24%; VI (optically pure material, α^{23}_{D} −5.62°, l = 1 dm.), 1.5%; VI (racemic material), 4.5%. The rotation of the homogeneous mixture was taken, α^{23}_{D} −0.083°, l = 1 dm. As a model for runs 5 and 6 the following synthetic mixture was prepared: III, 58%; IV, 6%; V, 23%; VI (optically pure material, α^{23}_{D} −5.62°), 13%. This mixture had a rotation of α^{23}_{D} −0.736°, l = 1 dm.

Runs 18 and 19 were carried out under identical conditions, so the procedure for run 19 will illustrate the method. The *p*-bromobenzenesulfonate of II (50 g.) was held at 30° in a solution prepared from 825 ml. of glacial acetic acid, 9.36 g. of K_2CO_3 (1 equiv. of carbonate per equiv. of sulfonate ester), and 38 ml. of acetic anhydride. At the end of 256 hours the solution was shaken with a mixture of 200 ml. of pentane, 200 ml. of pure ethyl ether and 1.5 liters of ice-water. The layers were separated and the aqueous layer was again washed with a 50% ether–pentane mixture (100 ml.). The organic extracts were combined, washed twice with 500-ml. portions of ice-water, once with a sodium carbonate solution, once again with water and dried. The solvent was evaporated through a short column under reduced pressure (the pot temperature never went over 30°), and the residue crystallized upon addition of cold pentane. Filtration of the crystalline mass produced the 1st crop of recovered sulfonate ester reported in Table VII. The filtrate was again concentrated under reduced pressure, and the residual oil was distilled at 0.1 mm. of pressure, the pot temperature never going over 80°. From the pot residue (non-acidic) was crystallized (upon the addition of a mixture of ether and pentane) the second crop of sulfonate ester reported in Table VII. The distillate (13.6 g.) was divided into two portions, runs 19 (continued) and 19a. In run 19, 10.6 g. of the distillate was dripped into a cooled, stirred mixture of 1.5 g. of lithium aluminum hydride and dry ether. The resulting mixture was cautiously mixed and shaken with ice, 6 *N* sodium hydroxide solution and pentane. The organic layer was washed with water, dried, and the solvent was evaporated through a short column (the pot temperature never rose above 100°). The residual oil was added to a basic alumina column (300 cm. long and 3 cm. in diameter) which had been prepared by allowing alumina (Harshaw activated alumina) to pass in a thin stream into pentane. The column was washed with pentane until olefin no longer appeared in the column filtrates. The column filtrates were combined, the pentane was evaporated through a short column (the pot temperature never rose above 100°), and the olefinic mixture was flash-distilled at 20 mm. pressure; wt. 0.51 g. This olefin was submitted directly to analysis.

The alcohol fraction which stayed on the column was eluted with pure methanol, and the methanol filtrate was evaporated through a short column to a volume of about 20 ml. This solution was shaken with pentane and water, the pentane layer was water-washed, dried, and the solvent was evaporated through a short column. The residue was flash-distilled at 1 mm. pressure, wt. 7.56 g., α^{21}_{D} −2.36° (l = 1 dm.). This alcohol was submitted directly to infrared analysis (see Table VII).

In run 19a, the acetate–olefin mixture (3.0 g.) was heated to 75° in dry glacial acetic acid for 36 hours and the products were isolated by the same procedure as outlined for run 19, the crystallization and distillation steps designed to eliminate sulfonate ester being omitted. The olefin obtained amounted to 0.33 g. and the alcohol, 1.77 g., α^{21}_{D} −2.14° (l = 1 dm.). This alcohol was used directly in the infrared analysis. To a sample of the alcohol was added 11% (by weight) of pure racemic 2-phenyl-2-butanol, and the rotation of the resulting mixture amounted to α^{21}_{D} −2.36°. To a second portion of the above alcohol was added 11% (by weight) of pure 2-phenyl-2-butanol rich by 7% in the (−)-isomer. The rotation amounted to α^{21}_{D} −2.59° (l = 1 dm.).

Decomposition of Sulfonate Esters in Acetonitrile.—Runs 12 and 13 were described in Paper V of this series.[1] The olefin fractions were isolated by a procedure analogous to that employed for runs 3–6.

Control Runs for the Olefinic Products of Solvolysis.—In runs 20 and 21 known synthetic mixtures of the 2-phenylbutenes (2.0 g.) were heated at 75° for 33 hours in a mixture of 500 ml. of glacial acetic acid to which 1.24 g. of anhydrous potassium carbonate and 20 ml. of acetic anhydride had been added. The procedure of isolation was identical to that used for runs 3–6, including the lithium aluminum hydride reduction and chromatographic steps. In run 20, n^{25}_{D} 1.5275 for the olefinic mixture before and n^{25}_{D} 1.5278 after the run; in run 21, n^{25}_{D} 1.5298 before and n^{25}_{D} 1.5303 after the run. The analyses of the olefinic mixtures are reported in Table V. The recovery of olefin amounted to 83% in run 20 and 77% in run 21.

In run 22 a mixture of 1 g. of 2-phenyl-1-butene (the most unstable of the four olefins), 2 g. of the *p*-toluenesulfonate of IB, 20 ml. of acetonitrile and 1 g. of anhydrous potassium acetate was held at reflux temperature for 39 hours. The olefin (0.93 g.) was recovered by the same procedure used in runs 12 and 13. The results of the olefin analysis are reported in Table V. The amount of V recovered is just what would be predicted if all that was put in survived.

In run 23, a mixture of 2 g. of olefin (see Table V), 825 ml. of glacial acetic acid, 38 ml. of acetic anhydride and 9.36 g. of potassium carbonate was held at 30° for 144 hours, and the products were isolated by the same procedure employed in runs 3–6. No alcoholic fraction was obtained, and an 82% recovery of olefin was realized.

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(23) All of the pentane used in this investigation was purified by fractionation on a sixty-plate column.

(24) The extinction coefficients of the three conjugated 2-phenylbutenes are around ten thousand in the region of 237–242 mμ (see ref. 2).

Preparation of 2-Acetoxy-2-phenylbutane.—A mixture of 7 g. of 2-phenyl-2-butanol,[25] 25 ml. of acetic anhydride and 10 ml. of pyridine was heated to 90° for 16 hours, and poured onto ice. The resulting mixture was extracted with pentane, the organic layer was washed with dilute sulfuric acid, with a sodium carbonate solution and with water. The pentane solution was dried, the solvent was evaporated and the residue was submitted to chromatographic absorption on an alumina column prepared in pentane. The column was first well washed with pentane, the column filtrates (which contained olefin) being discarded. The column was then washed with 1500 ml. of a 3% dry ether–97% pentane mixture. The solvent of the column eluate was evaporated and the resulting mixture was flash-distilled at 1 mm. of pressure, with the pot temperature below 90°; wt. 3.35 g., $n^{25}\text{D}$ 1.4943.

In another run the column filtrates from the 3% ether–97% pentane washes were cut into three fractions, the acetate being recovered separately in each case to give three samples, the indexes of refraction all being equal to $n^{25}\text{D}$ 1.4942. In a third run the starting tertiary carbinol was rich in the (−) isomer ($\alpha^{21}\text{D}$ −2.33°, l = 1 dm.); tertiary acetate having a rotation of $\alpha^{21}\text{D}$ −0.21° (l = 1 dm.) was obtained. A sample of 1.50 g. of this compound when reduced with lithium aluminum hydride in the usual fashion produced 2-phenyl-2-butanol, $n^{25}\text{D}$ 1.5163, $\alpha^{21}\text{D}$ −2.31° (l = 1 dm.). Apparently both the acetylation and reduction reactions are completely stereospecific.

Solvolyses of 2-Acetoxy-2-phenylbutane.—In run 24 a mixture of 2.0 g. of 2-acetoxy-2-phenylbutane and 180 ml. of glacial acetic acid and 5 ml. of acetic anhydride was held at 75° for 26 hours. The olefinic product was isolated by the same procedure used in runs 3–6, including the treatment with lithium aluminum hydride and the chromatographic separation steps. A total of 1.23 g. of olefin was recovered (Table V reports the analysis of this mixture).

Run 25 was carried out in the same fashion as run 24 except that the solvolysis mixture contained 1 mole of sodium acetate.

In run 26, 1.80 g. of tertiary acetate ($\alpha^{23}\text{D}$ −0.21°, l = 1 dm.) was mixed with 634 ml. of glacial acetic acid, 4.36 g. of potassium carbonate and 30 ml. of acetic anhydride, and the resulting mixture was held at 30° for 192 hours. The olefin and alcoholic fractions were then recovered as in runs 3–6 to give 0.036 g. of olefin and 0.95 g. of tertiary alcohol, $n^{25}\text{D}$ 1.5159, $\alpha^{21}\text{D}$ −1.78° (l = 1 dm.). In this experiment 77% of the original activity was retained.

When 2.0 g. of 2-acetoxy-2-phenylbutane was mixed with 100 ml. of acetonitrile, and the resulting solution was held at 82° for 64 hours, the starting tertiary acetate remained intact as shown by its almost quantitative recovery, $n^{25}\text{D}$ 1.4942.

Conversion of Olefinic Mixtures to Mixtures of Acetophenone and Propiophenone by Ozonolysis.—Commercial preparations (Eastman Kodak Co. White Label) of acetophenone and propiophenone were submitted to fractional distillation through a center-rod column (65 theoretical plates). Middle cuts were taken which had constant boiling points and indexes of refraction ($n^{25}\text{D}$ 1.5313 and 1.5248, respectively). These samples were employed in the preparation of Fig. 2.

Ozonolysis of an unknown olefinic mixture was carried out by passing ozone into an ice-cold solution of 1 g. of the olefin dissolved in 10 ml. of ethyl acetate until no more ozone was absorbed. The resulting solution was dripped into a stirred, boiling solution of 50 ml. of water, 1 g. of zinc dust and a trace of silver nitrate. After the addition was complete, the resulting mixture was filtered, and the filtrate was shaken with 25 ml. of ether. The water layer was again extracted with a small amount of ether, the ether extracts were combined, water washed, dried, and the solvent was evaporated through a short column. The residue was flash-distilled at 25 mm. of pressure to give from 0.56–0.68 g. of material. The distillate was mixed with 5 ml. of ethanol and freshly precipitated silver oxide (prepared by adding an excess of base to 1.5 g. of silver nitrate solution, and washing the precipitate repeatedly with first water and then ethanol), and this mixture was held at reflux temperature for one-half hour and filtered. The filtrate was shaken with pentane and water, the pentane layer was again washed with water, dried, and the solvent was evaporated through a short column. The residue was flash-distilled under 25 mm. of pressure to give from 0.35 to 0.48 g. of product. This material was used directly for the infrared analyses reported in Table IV.

Acknowledgment.—The author wishes to thank Dr. W. G. McMillan for several stimulating conversations concerning this work and Dr. G. S. Hammond for many helpful suggestions concerning the writing of the paper. He also wishes to thank Mr. W. Netusil for acquainting him with the operation of an infrared spectrophotometer.

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[25] This material was prepared by the addition of methyl magnesium iodide to propiophenone, the product being carefully fractionated at 100 mm. pressure. For the first and last drop of the major fraction of the distillate, $n^{25}\text{D}$ 1.5161.